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Modeling Impacts of Acid Precipitation for Northeastern Minnesota

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MODELING IMPACTS OF ACID PRECIPITATION FOR NORTHEASTERN MINNESOTA

by

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16. ABSTRACT

The acidification of lakes and streams due to acid precipitation has been documented in southern Sweden and Norway, the northeastern United States and southern Ontario. Geochemistry and regional lithology are recognized to be important factors in the susceptibility of lake ecosystems to acid precipitation. Local soils, glacial deposits and bedrock undergo biological and chemical weathering reactions to consume protons and release base cations - the greater is the total alkalinity production in the watershed, the greater is the capacity to neutralize acid loadings. Acid loadings are composed of wet and dry deposition to a watershed, and these are also important factors in the degree of acidification of lakes. A schematic of the trickle-down model, which is used in acid precipitation assessments, is shown in Figure 1.

The hydrology and geochemistry of the watershed determine the chemical weathering rate and thus are key factors in the susceptibility of lakes to acidification. In this chapter, lakes in northeastern Minnesota serve as case studies, where igneous bedrock and a lack of calcareous overburden are sufficient to classify the region as sensitive to acid rain. The volume-weighted acidity of precipitation pH ranges 4.6-4.85. These are threshold cases where it is not certain whether present acid loadings are acidifying lakes.

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Modeling Impacts of Acid Precipitation for Northeastern Minnesota.

A " Trickle-Down" mathematical model has been developed to assess impacts of acid precipitation, and it has been applied to lakes in northeastern Minnesota. In this chapter, field data are examined from a calibrated watershed at Filson Creek, Minnesota, and the trickle-down model is applied under time-varying conditions. A simplified, steady state version of the model is used to provide insight to the acid rain problem. The model allows prediction of lake response to increased acid loadings, but forecasts must be bracketed because of the uncertainty regarding chemical weathering rates.

INTRODUCTION

The acidification of lakes and streams due to acid precipitation has been documented in southern Sweden and Norway [1, 2, 3], the northeastern United States [4,5], and southern Ontario, Canada [6,7,8]. Geochemistry and regional lithology are recognized to be important factors in the susceptibility of lake ecosystems to acid precipitation [9,10,11,12,13]. Local soils, glacial deposits and bedrock undergo biological and chemical weathering reactions to consume protons and release base cations -- the greater is the total alkalinity production in the watershed, the greater is the capacity to neutralize acid loadings. Acid loadings are composed of wet and dry deposition to a watershed, and these are also important factors in the degree of acidification of lakes [14,15,16]. A schematic of the trickle-down model, which is used in acid precipitation assessments, is shown in Figure 1.

The hydrology and geochemistry of the watershed determine the chemical weathering rate and thus are key factors in the susceptibility of lakes to acidification. In this chapter, lakes in northeastern Minnesota serve as case studies, where igneous bedrock and a lack of calcareous overburden are sufficient to classify the region as sensitive to acid rain. The volume-weighted acidity of precipitation ranges from pH 4.6 - 4.85. These are threshold cases where it is not certain whether present acid loadings are acidifying lakes.

SITE DESCRIPTION

Filson Creek

Some 85 lakes within and near the Boundary Waters Canoe Area (BWCA), Minnesota, and the contiguous Voyageur's National Park (VNP), Canada, were sampled in November of 1978 [17]. Thirty-four of these lakes ranged from pH 6.3 - 7.0.

The Filson Creek watershed was studied intensively in 1979 with approximately weekly sampling at six locations of the Creek, including outflows from Bogberry and Omaday Lakes[18] (see Figure 2). The watershed is located in northeastern Minnesota at the southern edge of the BWCA in the Superior National Forest, a second-growth forest consisting of aspen, birch, spruce and conifers. Twenty-four percent of the total basin area of 24 km^2 is wetlands and lakes. Bedrock is gabbroic. Anorthite, augite, and olivine are the major minerals in the till. Deposits of glacial drift and Holocene surficial materials are generally less than 1.5 m thick, while exposed bedrock comprises 10-15 percent of the drainage basin. Dissolved organic acids contribute to the low pH of these highly colored waters.

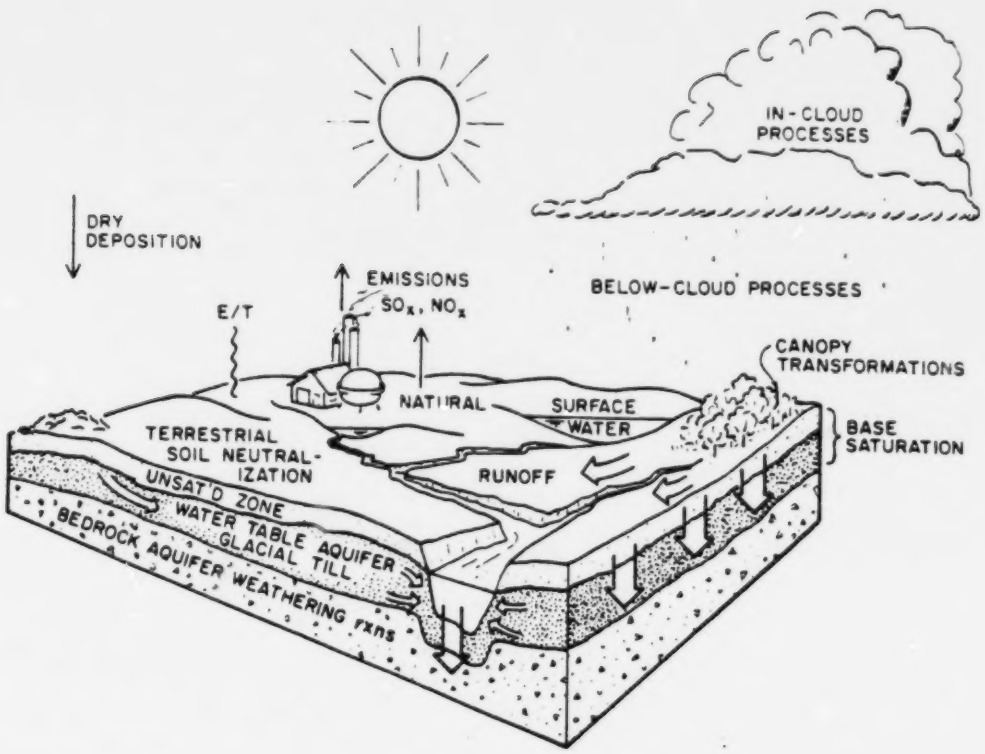

Figure 1. Schematic of Compartmentalized Fate and Transport Model for Acid Precipitation Assessments. Compartments include snowpack soil layer, unsaturated zone, water table aquifer, surface lakes and streams, and bedrock aquifers.

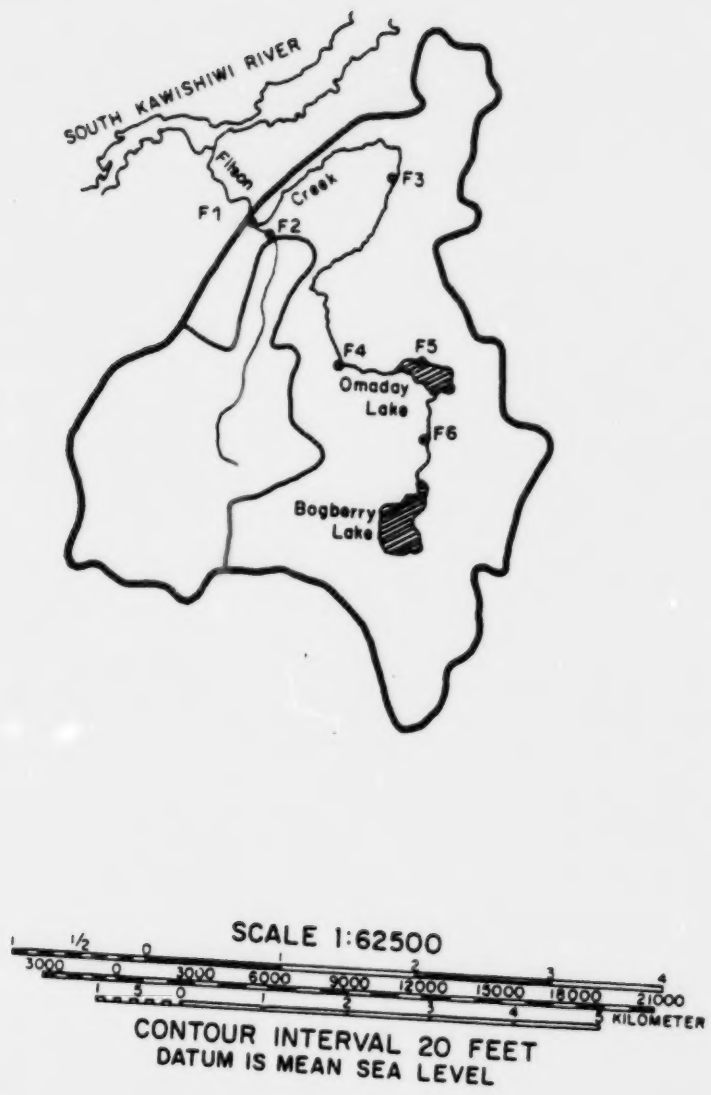

Figure 2. Filson Creek Watershed and Sampling Locations F1-F6.

MODEL DEVELOPMENT

To provide insight and simulations under different loading conditions, a "trickle-down" mathematical model was developed, based on the principle of continuity of mass within a compartmentalized volume. Alkalinity is a conservative state variable which is not influenced by the exchange of carbon dioxide with the atmosphere. Negative alkalinity is free mineral acidity. Chemical weathering reactions of H^+ and $CO_{2(aq)}$ with minerals (e.g. augite, feldspars, hornblende, biotite, and olivine) are congruent and incongruent dissolutions which consume protons and release principally Ca^{+2}, Mg^{+2}, Fe^{+2} and Na^+.

The alkalinity mass balance model consists of an open system of CO_2 and H_2O which undergoes strong acid and base titration. Nitrification by soil micro-organisms, sulfide oxidation, base cation uptake by vegetation, and soil cation exchange comprise strong acid additions. Denitrification, desulfurization, sulfate adsorption by soil, nitrate uptake by vegetation, and chemical weathering represent processes that could add strong base to the system. All of these processes are presently lumped into one kinetic formulation for each compartment. To consider the effects of each process individually would require the inclusion of the major cations and anions as state variables. If details are known regarding base cation denudation and nutrient cycling in the watershed, then the neutralization rate can be apportioned among various processes. In the Minnesota and Wisconsin lakes, chemical weathering likely predominates since cationic export is approximately

equal to the net neutralization rate (alkalinity inputs minus outflows from the watershed.)

The system of mass balances for each compartment is presented in Equations 1 - 6. It is necessary to couple this mass balance of alkalinity with a water balance, based on field measurements and hydraulic modeling.

SNOW COMPARTMENT 1
$$\frac{d(V_1A_1)}{dt} = -LB_1 + Q_{1,0}A_0 - Q_{2,1}A_1 \quad (1)$$

SOIL COMPARTMENT 2
$$\frac{d(V_2A_2)}{dt} = Q_{2,1}A_1 - LB_2 + Q_{2,0}A_0 - Q_{4,2}A_2 - Q_{3,2}A_2 + k_2M_2V_2(r_{eq2} - r_2)/\varepsilon_2 \quad (2)$$

UNSATURATED COMPARTMENT 3
$$\frac{d(V_3A_3)}{dt} = Q_{3,2}A_2 - Q_{5,3}A_3 - Q_{4,3}A_3 + k_3M_3V_3(r_{eq3} - r_3)/\varepsilon_3 \quad (3)$$

SURFACE WATERS COMPARTMENT 4
$$\frac{d(V_4A_4)}{dt} = Q_{4,2}A_2 + Q_{4,5}A_5 - Q_{7,4}A_4 + Q_{4,3}A_3 + Q_{4,1}A_1 + k_4M_4V_4(r_{eq4} - r_4)/\varepsilon_4 - LB_4 + Q_{4,0}A_0 - Q_{5,4}A_4 \quad (4)$$

WATER TABLE AQUIFER COMPARTMENT 5
$$\frac{d(V_5A_5)}{dt} = Q_{5,3}A_3 - Q_{4,5}A_5 + k_5M_5V_5(r_{eq5} - r_5)/\varepsilon_5 + Q_{5,4}A_4 - Q_{6,5}A_5 - Q_{7,5}A_5 + Q_{5,6}A_6 \quad (5)$$

BEDROCK AQUIFER COMPARTMENT 6
$$\frac{d(V_6A_6)}{dt} = Q_{6,5}A_5 - Q_{5,6}A_6 - Q_{7,6}A_6 + k_6M_6V_6(r_{eq6} - r_6)/\varepsilon_6 \quad (6)$$

t = time, yr

V = water volume in each compartment, m^3

A = alkalinity in each compartment, $\mu eq/l$

$Q_{x,y}$ = flowrate from compartment y to compartment x, m^3/yr

L = dryfall acid laoding, eq/ha-yr as H^+

k = rate constant for acid neutralization by soil or sediments, 1/yr

M = bulk density of the soil or sediments, kg/m^3

ϵ = moisture content, m^3 H_2O/m^3

r_{eq} = initial sum of the exchangeable bases on the soil, eq/100kg

r = cumulative base cation export (eq. of acid neutralized), eq/100kg

β_1 = snow-covered area, ha

β_2 = exposed terrestrial area, ha

β_4 = surface area of lakes, ha

The seventh compartment refers to export out of the watershed, while the zero compartment is from atmospheric and throughfall precipitations. If snow cover does not exist, throughfall precipitation is input directly to the soil compartment. Percolation is rapid in these porous soils, so overland runoff is neglected unless the soil is frozen. The rate constant for weathering reactions, k, is a function of inverse detention time and hydrogen ion concentration to some fractional power, the result of correlations developed in the field or laboratory studies. According to laboratory experiments [19,20], chemical weathering rates should be directly proportional to some fractional power of the hydrogen ion concentration.

To examine the role of hydrology and neutralization rates more closely for the large number of Wisconsin and Minnesota lakes, Equations 1 - 6 were summed and

averaged over an entire watershed. Thus the mass of alkalinity in a single lake, assuming complete mixing and steady flow, is given by Equation 7.

$$V \frac{dA}{dt} = - I L_{acy} (1-f) - QA + kV \qquad (7)$$

where L_{acy} = acidity of precipitation, μeq/l

I = precipitation volume, l/yr

Q = outflow rate, l/yr

k = zero order neutralization rate by sediments, μeq/l-yr

f = fraction of acid neutralized in the watershed

Equation 7 admits the following solution:

$$A = A_o e^{-Qt/V} + (\frac{kV}{Q} - \frac{I}{Q} L_{acy}(1-f))(1-e^{-Qt/V}) \qquad (8)$$

with the steady state asymptote:

$$A = \frac{kV}{Q} - \frac{I}{Q} L_{acy} (1-f) \qquad (9)$$

The steady state alkalinity concentration of a lake consists of alkalinity inputs due to neutralization reactions of the sediments, k, and due to neutralization of acid precipitation in the watershed, f. For many lakes with watershed areas greater than surface areas, it is possible to neglect the first term of Equation 9.

FILSON CREEK FIELD STUDIES

Hydrology

An estimate of the annual average water balance for the watershed is depicted in Figure 3. The water budget is preliminary and is based on measured baseflow (0.7 cfs), estimated annual average runoff (4cfs), average precipitation (74 cm) and average evaporation (61 cm). A small amount of recharge to groundwater is expected to occur in the littoral regions of the lakes(300 m^3/day), and some discharge of groundwater to the creek is estimated based on water chemistry data (1712 m^3/day).

Figure 4 is the hydrograph for the outflow of the Filson Creek watershed in 1979. Flow was recorded at a United States Geologic Survey (USGS) gaging station F1, at the outflow from the watershed. Baseflow was estimated to be approximately 0.7 cfs, although the lowest flow recorded was 0.2 cfs in August of 1979. 1979 was a relatively wet year with a total cumulative runoff of 5.74×10^6 m^3 during the period from 16 March to 31 July, 1979, which accounted for greater than 90% of the cumulative flow during the water year 1979. The measured flow at F1 during this period amounted to about 23 cm of precipitation distributed over the entire watershed.

The water budget for 1979 is shown in Table 1. Most of the water in the first snowmelt was not measured at F1 but either was stored in the upstream wetlands or flowed over ice. The volume of the first snowmelt water would have been sufficient to raise the level of the wetlands approximately 19 cm, a little large compared with observation wells. The second snowmelt greatly increased streamflow at F1; apparently most of the available storage was filled by the first

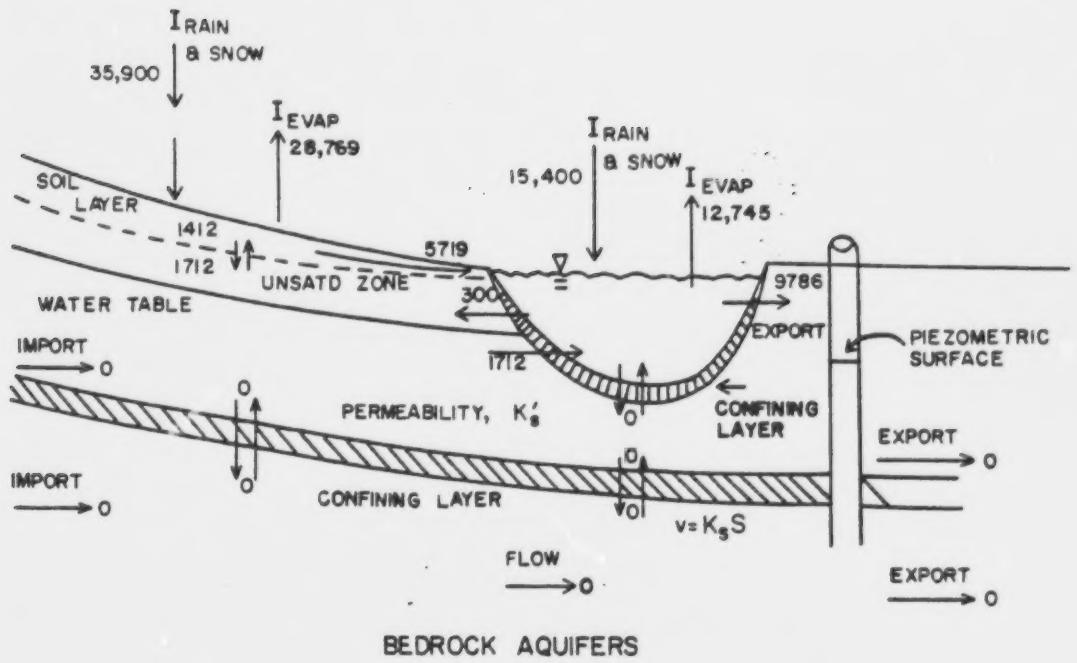

Figure 3. Estimated Annual Average Hydrologic Balance for the Filson Creek Watershed (in m^3/day).

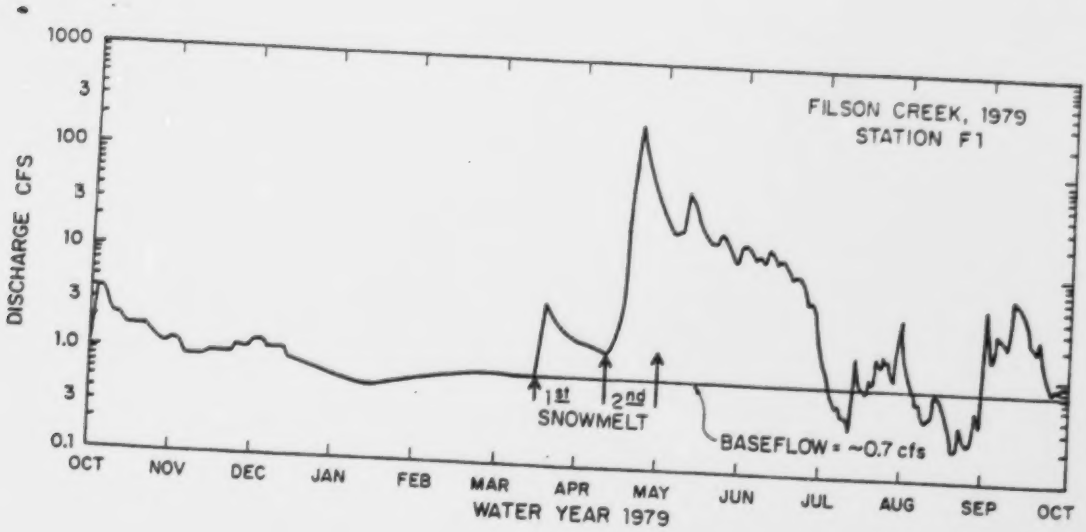

Figure 4. Hydrograph at Station F1, 1979.

Table 1. Hydrologic Balance For Filson Creek, 1979

STORAGE + EVAP = SNOWMELT + PRECIP - OUTFLOW

(in cubic meters)

	PERIOD		
	First Snowmelt 3/16 - 4/10/79	Second Snowmelt 4/11 - 4/30/79	TOTAL* 3/16 - 7/31/79
SNOWMELT			
Total in Snowmelt	1.5×10^6	2.1×10^6	3.7×10^6
Coniferous	(3.9×10^5)	(8.0×10^5)	
Deciduous	(5.3×10^5)	(6.6×10^5)	
Open	(6.2×10^5)	(6.6×10^5)	
PRECIP			
Precip. during Runoff Period	1.4×10^6	1.8×10^6	$> 3.6 \times 10^6$
OUTFLOW			
Cumulative Flow Measured at F1	8.2×10^4	3.0×10^6	5.7×10^6
CALCULATED STORAGE + EVAP	2.8×10^6	0.9×10^6	$> 1.6 \times 10^6$

* Total observations at station F1 were from 3/16/79 - 7/31/79.

However, precipitation collector was only recorded through 5/26/79.

snowmelt. From 16 March to 31 July, the total volume of water which passed the gage at F1 was ~ 22% less than the estimated precipitation volume of snowpack (3.7×10^6 m^3) plus rainfall (3.7×10^6 m^3). The difference reflects losses of water from the watershed, principally evaporation, and possibly some storage through the year.

Chemistry

pH Prediction

It is possible to predict pH in many dilute waters by assuming an open system of CO_2 and H_2O, titrated with a strong acid or strong base. This is a surprisingly simple model which accounts for pH in natural waters as a result of CO_2 and hydrogen ion weathering of mineral bases.

Some of the total alkalinity in bog lakes is due to organic acid anions which are protonated in an alkalinity titration. These acids come from biological processes and are leached from soils by groundwater. As much as 70 percent of the total alkalinity in highly colored Omaday Lake, Minnesota, is attributable to organic acid anions. Equilibrium pH is decreased due to the presence of the acids. For the purpose of calculating pH, we define the following:

$$\text{Total } \{A\} = \{HCO_3^-\} + 2\{CO_3^{-2}\} + \{OH^-\} - \{H^+\} + \{B^-\} \quad (10)$$

$$\text{Carbonate } \{A\} = \{HCO_3^-\} + 2\{CO_3^{-2}\} \quad (11)$$

where $\{B^-\}$ = activity of organic acid anions or generalized weak base

The final calculation of pH can be made from Equation 12 below:

$$\{A\} = K_H(\alpha_1 + 2\alpha_2)(pCO_2/\alpha_o) + \{OH^-\}-\{H^+\}+\{B^-\} \quad (12)$$

in which:

$\{A\}$ = total alkalinity

K_H = Henry's law constant for CO_2

α_o = $\{H_2CO_3\}/C_T$ = distribution coefficient

α_1 = $\{HCO_3^-\}/C_T$ = distribution coefficient

α_2 = $\{CO_3^{-2}\}/C_T$ = distribution coefficient

pCO_2 = partial pressure of CO_2 = $10^{-3.5}$ at 1 atm total pressure

Shane [21] derived a fourth-order polynomial expressing hydrogen ion concentration in terms of alkalinity and CO_2 acidity. To arrange this into terms of alkalinity and CO_2 partial pressure, it was expanded to the following fifth-order polynomial:

$$T_5(H^+)^5 + T_4(H^+)^4 + T_3(H^+)^3 + T_2(H^+)^2 + T_1(H^+) + T_0 = 0 \quad (13)$$

where:

$T_5 = 1.0$

$T_4 = A + K_1$

$T_3 = K_1K_2 - K_1K_hpCO_2 + AK_1 - K_w$

$T_2 = -K_1(2K_2K_hpCO_2 - AK_2 + K_1K_hpCO_2 + K_w)$

$T_1 = -K_1K_2(K_w + 3K_1K_hpCO_2)$

$T_0 = -2K_1^2K_2^2K_hpCO_2$

K_1 = first ionization constant for carbonic acid

= $1 \times 10^{-6.30}$

K_2 = second ionization constant for carbonic acid
= $1 \times 10^{-10.25}$

K_w = ionization constant for water
= $1 \times 10^{-14.00}$

In the computer program, this equation was solved for any given alkalinity and CO_2 partial pressure by a trial-and-error method since only the single root within the pH range 0 to 14 was needed.

Figure 5 shows the Filson Creek measurements do not fit Equation 12 unless a substantial portion of the total alkalinity exists as organic conjugate base anions (B^-). If $pCO_2 = 10^{-2.7}$ (sixfold supersaturated) and if the organic acid concentration is $10^{-4.2}$ M (with a pKa of approximately 4.5), then Equation 12 fits the field data reasonably well. Supersaturation of CO_2 is likely due to microbial respiration in these colored waters.

Ion Balance

It was difficult to obtain a tight ion balance (electroneutrality) calculation for the Filson Creek. Considering alkalinity as anions in the calculation, the method was consistently "short" on anions. The mean error and standard deviation were 24.7 ± 5.0 %.

One explanation would be that some organics existed as anions which were not included in the alkalinity titration. Alternatively, some of the cations could be complexed by organics and exist as neutral species or colloidal solids. Iron and manganese might exist as precipitates or adsorped to finely-divided oxide surfaces.

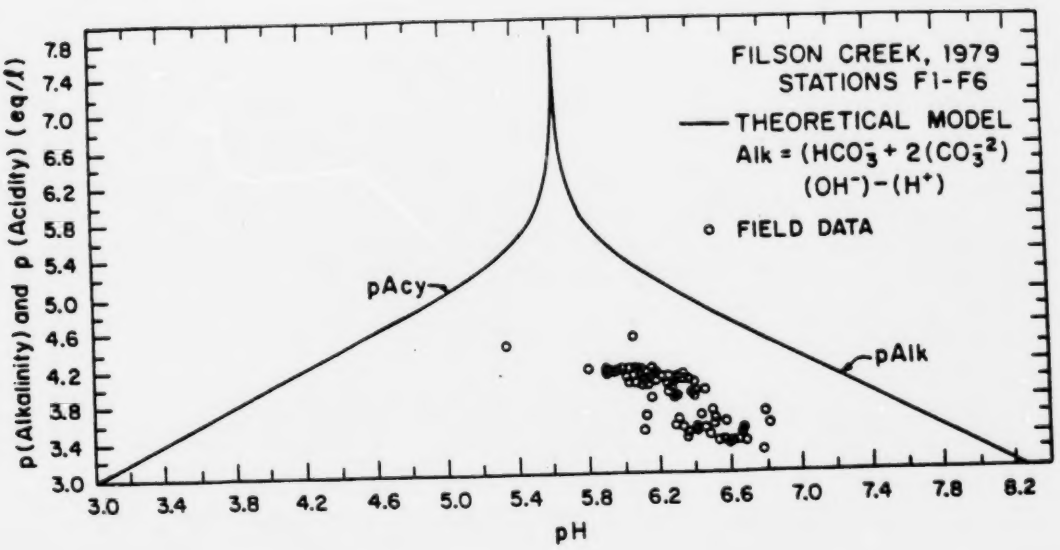

Figure 5. Plot of pAlk vs. pH for Filson Creek, 1979. Solid line is model Equation 12 assuming $(B^-)=0$ and $pCO_2=10^{-3.5}$. The field data approach Equation 12 if $(B^-)=10^{-4.2}$M and $pCO_2=10^{-2.7}$.

Chemical Budgets

Table 2 shows the sulfate budget for the Filson Creek watershed. A mass of 7.5 kg/ha was measured at Station F1 over the period from 16 March - 7 June, 1979, which represented most of the annual export from the watershed. Sulfate export during the period was a little less than the total sulfate loading of ~ 11 kg/ha-yr, according to Glass and Loucks [17]. It is possible that there was production of sulfate in the basin by sulfide oxidation and/or some anaerobic desulfurization.

The amount in precipitation, 2.32 kg/ha, was small because only 10 weeks of a year were measured. Annual sulfate loadings in bulk precipitation could approach 10 kg/ha-yr. It seems that a portion of the sulfate that was exported from the watershed during the spring months was from "stored sources". Dry deposition of sulfate and SO_2 is known to be highest in the summer months, and perhaps it was stored in the soil. The sum of the sulfate in snowpack and rainfall (4.1 kg/ha) was less than that measured at the outflow at F1 (7.5 kg/ha) during the spring months. However, considerable sulfates entered the watershed via rainfall during an unmeasured period from 11 May - 7 June, 1979.

Contrary to the behavior of sulfate in the watershed was nitrate. Nitrate (NO_2-N + NO_3-N) exports from the Filson Creek watershed amounted to only 370 kg in a 68 day period or roughly 0.1 kg/ha. This was smaller than the 0.29 kg N/ha-yr reported by Glass and Loucks [17]. Nitrate concentrations in snowpack were roughly 0.8 kg/ha, so nitrate was not conserved. Loss of nitrate could be due to plant uptake and denitrification in poorly drained soils.
Nitrate concentrations increased at the very initial stages of snowmelt, but high concentrations during the fall and winter were likely due to snowmelt and

Table 2. Sulfate Budget for Filson Creek (kg/ha)

STORAGE = SNOWMELT + PRECIP - OUTFLOW

(kg/ha)

SNOWMELT	
Total in Snowpack	1.76
Coniferous	(1.45)
Deciduous	(1.74)
Open	(2.20)
PRECIP	
Total in Precip.[+] (excluding snowpack)	> 2.32
Event = 20 April, 1979	(0.76)
Event = 11 May, 1979	(1.56)
OUTFLOW	
Cumulative Mass[*] Measured at F1	7.5

* Σ(conc. x Flow) from 16 March - 7 June, 1979

+ Measured from 16 March - 11 May, 1979

nitrified soil water percolating into Filson Creek.

The toxic metals copper and aluminum were measured in significant concentrations, and their export totals were calculated. Copper exports amounted to 0.009 kg/ha over a 68 day period from 19 March - 25 May, 1979. These exports were significantly larger than one would expect from snowpack inputs alone. Weathering of Cu-sulfide minerals is a probable cause. The amount exported was more a function of flow than concentration. Copper concentrations did not change drastically in space or time and ranged from 0.005 - 0.012 mg/l.

Aluminum exported from the basin amounted to 0.3 kg/ha for the period from 19 March - 25 May, 1979. Aluminum concentrations ranged from 0.10 - 0.40 mg/l and did not vary much in space or time. The amount exported increased during high flow periods. It is likely that the aluminum existed as organic complexes.

Time Series

A time series plot of selected chemical constituents leaving the Filson Creek watershed during 1979 is given in Figure 6. It can be shown that sulfate concentrations were highest from mid-April to mid-May. However, increased nitrate concentrations corresponded to the snowmelt and the decline in alkalinity and pH most closely. The increase in anions during snowmelt was nearly 100 μeq/l. Alkalinity decreased from a maximum of 458 μeq/l to a minimum of 67 due to the increase of HNO_3 and H_2SO_4 and especially due to dilution of bicarbonate with snowmelt water. Alkalinity recovered somewhat later than pH, perhaps due to the influence and relative importance of organic acids.

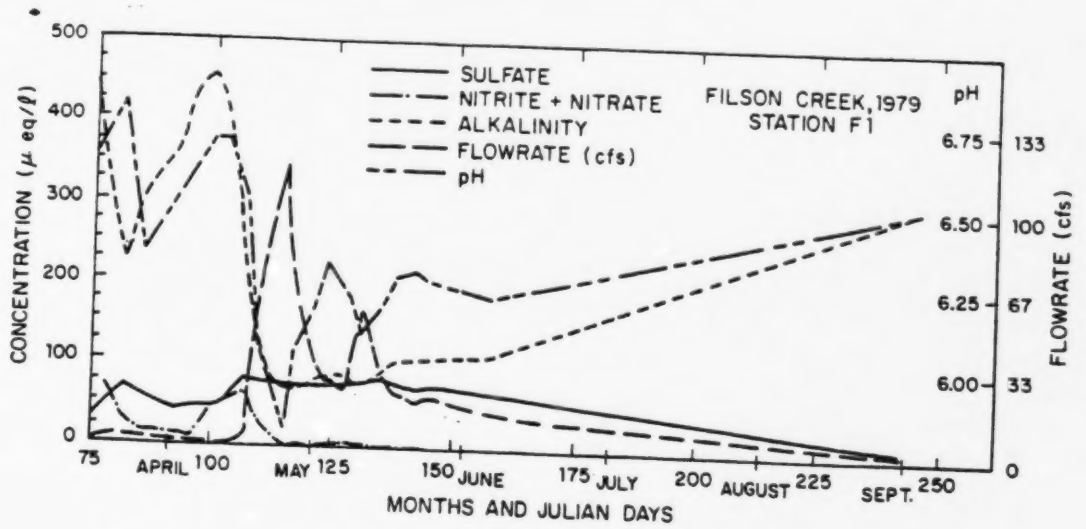

Figure 6. Time Series of Selected Chemical Constituents Leaving the Filson Creek Watershed, 1979.

Base metal cation concentrations during 1979 are shown in Figure 7. Winter concentrations of total Ca, Mg, and Fe were high due to groundwater inputs of weathering products. Spring and summer concentrations were lower due to dilution by precipitation runoff and vegetational uptake. The high magnesium and iron concentrations reflected olivine ($(Mg, Fe)_2SiO_4$) weathering in the till; calcium likely emanated from anorthite (Ca-plagioclase, $CaAl_2Si_2O_8$) weathering; and sodium came from albite ($NaAlSi_3O_8$)

The net effect of the incongruent dissolution of feldspars is shown below for anorthite as an example[22] .

$$CaAl_2Si_2O_8(\text{anorthite}) + 2\ H^+ \rightarrow 2\ Al(OH)_{3(s)} + Ca^{+2} + 2\ H_4SiO_4$$

$$2\ Al(OH)_{3(s)} + 2\ H_4SiO_4 \rightarrow Al_2Si_2O_5(OH)_4(\text{kaolinite}) + 10\ H_2O$$

$$\text{anorthite} + 2\ H^+ \rightarrow Ca^{+2} + \text{kaolinite} + 5\ H_2O$$

Hence chemical weathering serves as a strong base titration of percolated water, in which hydrogen ions are sorbed and calcium ions are released.

Longitutinal Stream Concentrations

Figures 8, 9, 10 show the concentrations of alkalinity, pH, and dissolved organic carbon in Filson Creek for 1979. Stations F6 and F4 correspond to the outlets of Bogberry and Omaday Lakes, respectively. The minimum pH was recorded on April 20 (Day 110) at station F4. Recovery of pH was relatively rapid and essentially complete by May 25 (Day 145). However, alkalinity remained low on May 25, possibly due to a reduced amount of organic acid anions which were titrated as alkalinity. Alkalinity on April 20 (Day 110) gradually increased with distance downstream from 32 to 100 μeq/l, indicating a degree of chemical weathering during transit. The increase in calcium and

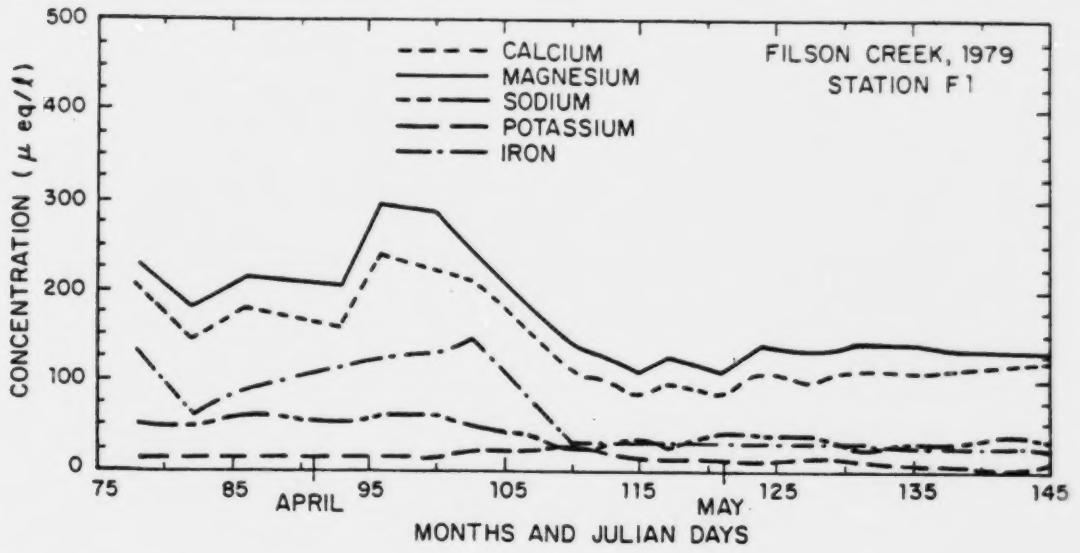

Figure 7. Base Cation Concentrations Leaving Filson Creek Watershed, 1979.

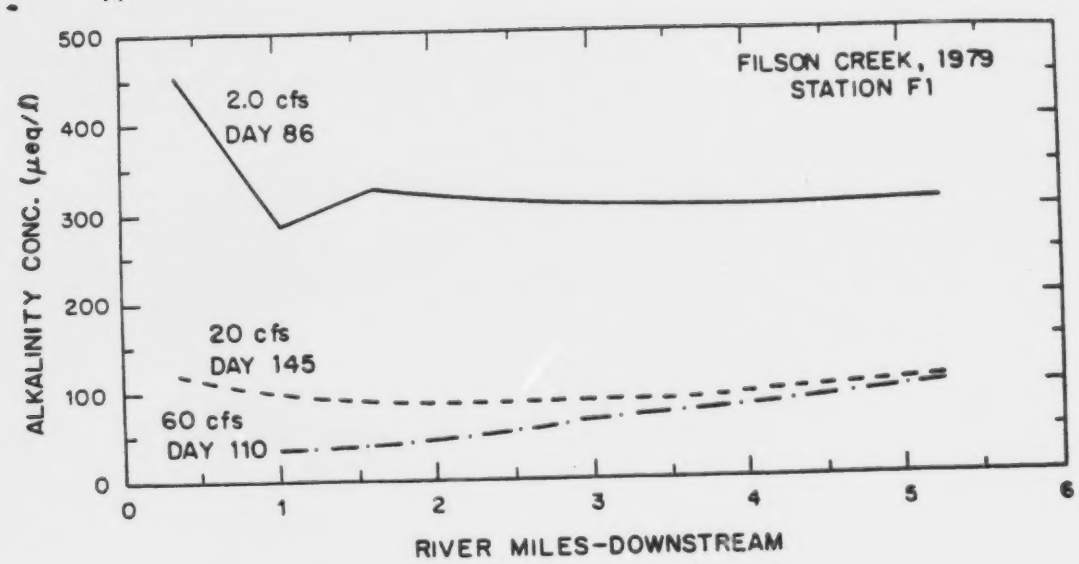

Figure 8. Alkalinity vs. Longitudinal Distance.

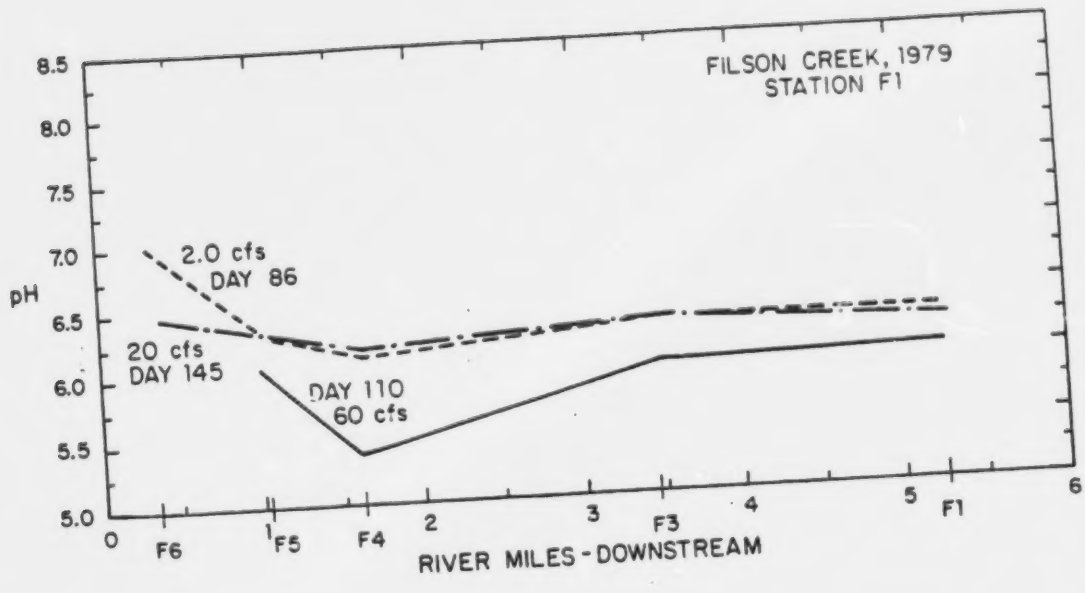

Figure 9. pH vs. Longitudinal Distance.

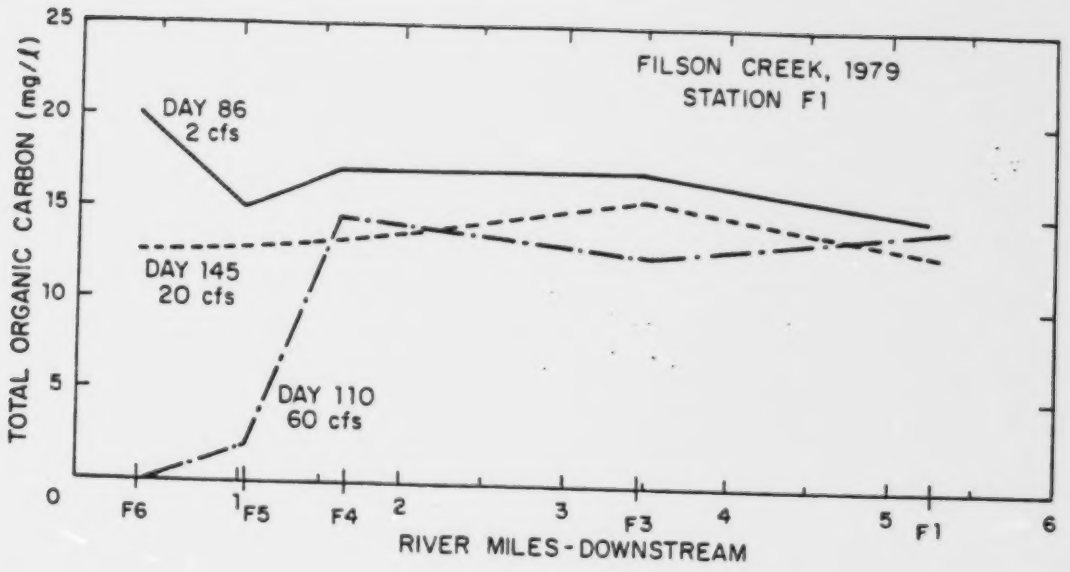

Figure 10. Dissolved Organic Carbon vs. Longitudinal Distance.

magnesium (from 132 to 249 μeq/l) was more than enough to account for the alkalinity increase.

Dissolved organic carbon increased from almost zero to 14 mg/l on Day 110 during transit from station F6 to F1. Indications are that streamwater at F6 and F5 contained a relatively small contribution from organic soil water. By Day 145, the organic carbon was present in all samples at greater than 10 mg/l, but it was not as concentrated as samples from Day 86 and perhaps did not contain the same fraction of organic acids.

Sampling of lake and streamwater during snowmelt events was difficult due to stratification of slightly warmer snowmelt water over older streamwater, so samples were obtained as a depth integral.

Weathering Rates

Total ionic denudation in the watershed consisted of weathering and incorporation of base cations into an aggrading canopy, as well as export of base cations in stream discharge. An inverse relationship between base cation concentrations and flowrate at station F1 is shown in Figure 11. The sum of the base cations (demudation concentration) was strongly correlated to inverse flow in 1979. The longer was the residence time of water in the soil and mineral till, the greater was the cation concentration.

Likewise Figure 12 shows that alkalinity increased significantly as flowrate decreased. Alkalinity was a stronger function of inverse flow than was base cation concentration. Other sources of bases may be important in the watershed, especially during low flow periods. Denitrification, desulfurization,

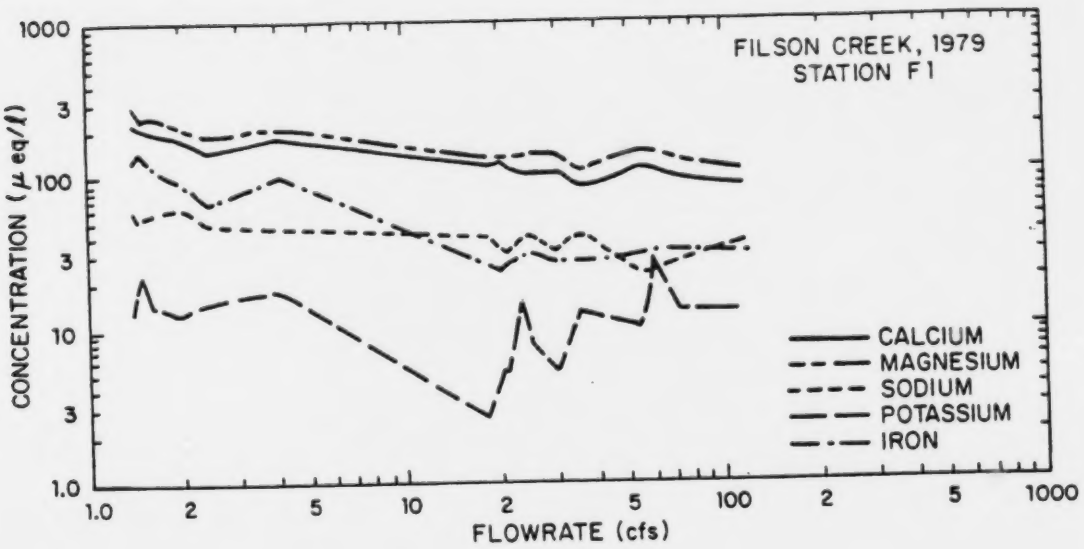

Figure 11. Correlation Between Base Cation Concentrations and Flowrate. log Q = -4.159 log(Ca+Mg+Na+K+Fe) + 11.861; r=0.942

sulfate adsorption, and nitrate uptake may be important processes which can release bases. Sulfate concentration decreased moderately with increasing flowrate, while nitrate displayed a weak, inverse relationship with flowrate (Figure 12).

Figure 13 gives the export of base cations as a function of flowrate. Chemical weathering and total neutralization rates were strongly a function of flowrate. According to Figure 13, a ten-fold increase in flow results in approximately a six-fold increase in base cation export. This is important because it relates watersheds with differing precipitation volumes and identical pH of bulk precipitation. Another interpretation is that "wet" years should produce the most critically low pH in streamwater, but not greatly so, because base cation export would also increase.

At the mean annual discharge rate of 4 cfs, the base cation export (weathering) is 0.055 eq/sec or approximately 700 eq/ha-yr. This results in an average alkalinity of about 200 μeq/l in the watershed.

MODELING RESULTS

Filson Creek

Figure 14 shows the results of a model calibration for Filson Creek based on field measurements of water chemistry and hydrology. The marked decrease in alkalinity and pH from day 100-125 was due to snowmelt and dilution of alkalinity, coupled with the rapid runoff of free mineral acids (sulfate and nitrate). Further depression of the pH was averted due to two important

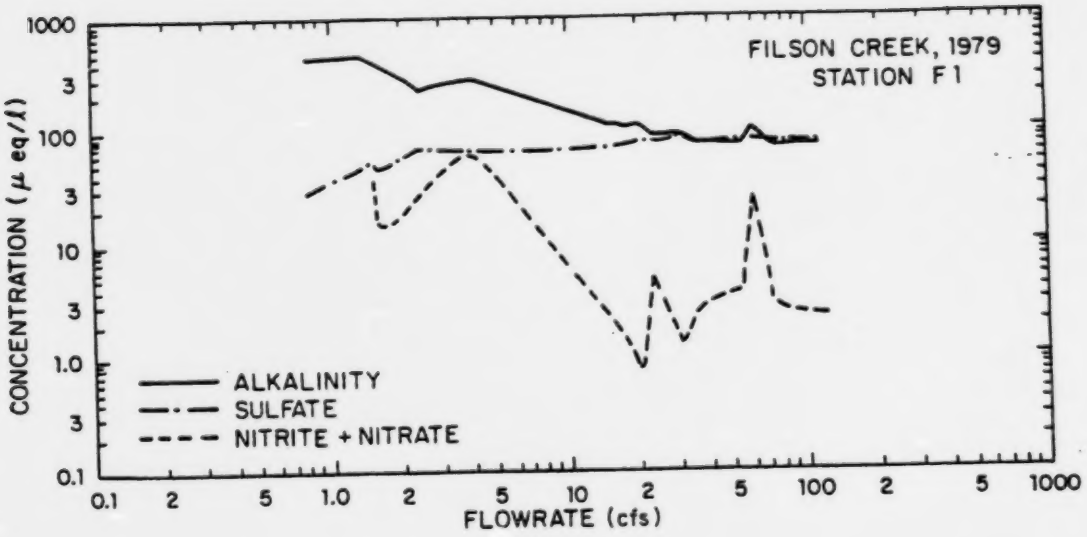

Figure 12. Anion Concentrations as a Function of Flowrate.
$\log Q = -2.106 \log(Alk) + 5.601$; r=0.968
$\log Q = +4.769 \log(SO_4) - 7.559$; r=0.817

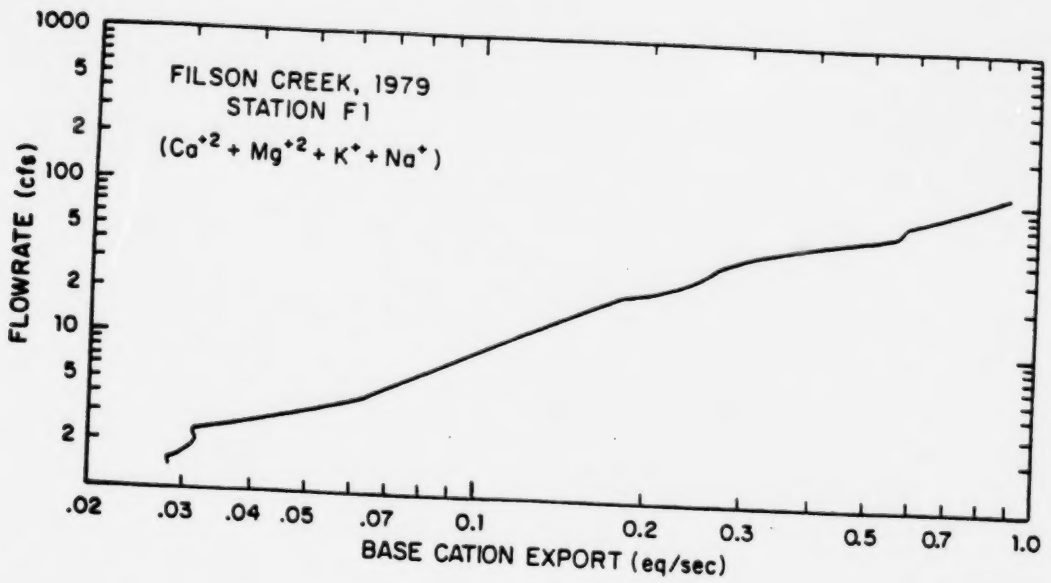

Figure 13. Export of Base Cations as a Function of Flowrate
log Q = +1.259 log(Export in ueq/sec) - 5.372; r=0.995

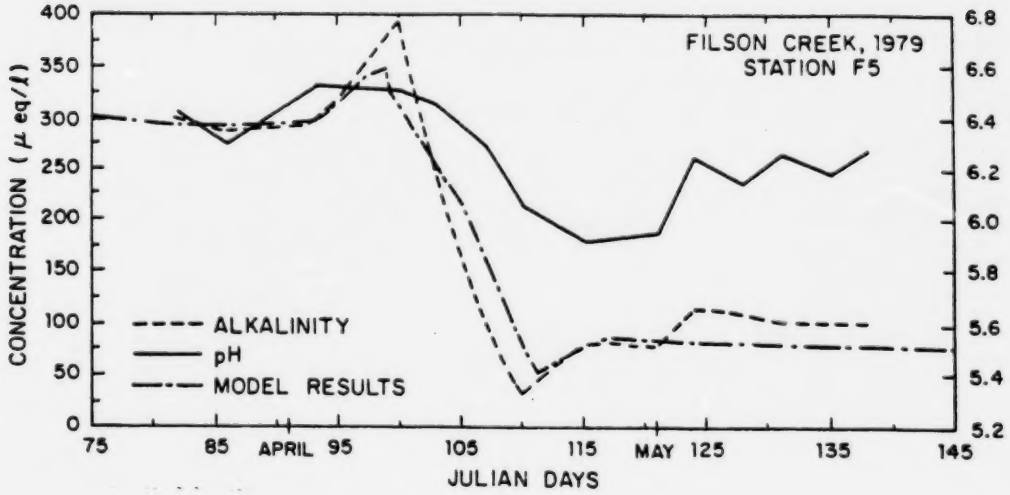

Figure 14. Trickle-Down Model Results for the Surface Water Compartment of Filson Creek during a Snowmelt Event, Subcatchment above Station 5, 1979.

factors: 1) storage and dilution of acidified snowmelt water in wetlands and bogs, and 2) buffering by conjugate bases of the organic acids in these colored waters. Model equations 1 - 6 have proven to be a useful description of the worst case snowmelt event. Average model coefficients are given in Table 3 for the entire watershed.

It is possible to use the trickle-down model with annual average acid depositional loadings for long term simulations. The results of a twenty-year simulation are presented in Table 4. With a wet precipitation acid loading of 106 eq/ha-yr (pH 4.85) and a dry acid loading of 15 eq/ha-yr, the steady state solution to equations 1 - 6 is given at YEAR 0 in Table 4. The surface water pH was 6.2 and alkalinity was 53 μeq/l, most of which was contributed by organic acid anions. The soil pH was 5.8 at YEAR 0. After a doubling in acid deposition to 242 eq/ha-yr, a large decrease is predicted in soil water and surface water pH. Of the alkalinity remaining in the surface water, most is contributed by organic acid anions. During this simulation, about two percent of the bases in the soil layers were consumed -- i.e., the base saturation decreased. However, if the neutralization rate constant would increase with increasing acid deposition, then more bases would be released from the soil and unsaturated zone by ion exchange and chemical weathering.

Table 3. Filson Creek Watershed Average Environmental Parameters for Trickle-Down Model (maximum snowpack water = 3.26×10^6 m^3; Organic Acids = 4.5×10^{-5} M)

	Soil	Unsatd. Zone	Surface Water	Aquifer
Water Volume, m^3	1.08×10^6	7.06×10^6	3.78×10^6	2.52×10^8
Environmental Vol., m^3	1.08×10^7	1.40×10^7	N.A.	2.52×10^9
Soil Density, kg/m^3	1.55×10^3	1.40×10^3	N.A.	1.55×10^3
Neutralization Rate Constant, day^{-1}	2.5×10^{-6}	3.3×10^{-6}	N.A.	8.8×10^{-7}
Sum of Bases, eq/kg	0.05	0.06	N.A.	0.001

Table 4. Twenty Year Simulation with Double the Present Acid Deposition and Constant Weathering Rate, Filson Creek Watershed

	Soil[1]		Unsatd. Zone[2]		Surface Water[3]		Aquifer[4]	
YEAR	Alk.*	pH	Alk.*	pH	Alk.*	pH	Alk.*	pH
0	8.7	5.8	125	6.89	53	6.2	325	6.8
1	-9.5	5.0	125	6.89	44	5.5	325	6.8
2	-11.3	4.9	124	6.89	38	5.1	325	6.8
3	-11.4	4.9	122	6.88	36	5.0	325	6.8
4	-11.4	4.9	121	6.88	35	5.0	325	6.8
5	-11.4	4.9	121	6.88	35	5.0	325	6.8
10	-11.4	4.9	117	6.86	35	5.0	325	6.8
20	-11.4	4.9	113	6.85	35	5.0	325	6.8

* Total Alkalinity in μeq/l

[1] $pCO_2 = 10^{-3.0}$ atm

[2] $pCO_2 = 10^{-3.0}$ atm

[3] $pCO_2 = 10^{-3.5}$ atm, Org. Acids = 4.5×10^{-5} M

[4] $pCO_2 = 10^{-2.5}$ atm

SUMMARY

The trickle-down mathematical model was successfully calibrated with field data from Filson Creek, Minnesota. Even though acidic loadings were moderate at Filson Creek (pH 4.8 of bulk precipitation and a sulfate load of 11 kg/ha-yr), a substantial pH depression was observed during snowmelt. Simulations indicated that the average spring pH of Filson Creek would decrease from 6.2 to 5.0 if acidic deposition increased two-fold. The largest uncertainty in forecasting lake response to increased acidic loadings was the kinetics of chemical weathering. Hydrologic flowrates and chemical weathering rates were most sensitive parameters in their effect on surface water pH in the trickle-down model.

ACKNOWLEDGMENTS

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